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Effect of Copper on the Corrosion of High-Purity  
Aluminum in Hydrochloric Acid

M. Metzger, G.R. Ramagopal and O.P. Arora

Department of Mining and Metallurgical Engineering  
University of Illinois, Urbana, Illinois

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# Effect of Copper on the Corrosion of High-Purity Aluminum in Hydrochloric Acid

M. Metzger, G.R. Ramagopal and O.P. Arora

## I. Introduction

Studies of intergranular corrosion in single-phase high-purity aluminum exposed to hydrochloric acid<sup>1</sup> led to the investigation of general corrosion described here. This work is closely related to the intergranular corrosion work but is more appropriately presented first and by itself. The corrosion rates of high purity metal are moderate ones, rather than the high rates expected from thermodynamic data, because of the presence of a protective film; with this strongly inhibited situation, corrosion reactions are sensitive to the structure and composition of the specimen and the system is therefore one where some of the metallurgical factors in corrosion are readily recognized and studied. Although much remains to be learned about specific mechanisms, the broader aspects of the corrosion of aluminum are reasonably well understood<sup>2</sup>.

The relation between composition and general corrosion for purer grades of aluminum received considerable attention in earlier work<sup>3,4,5</sup>, dealing with hydrochloric acid and other media. It was recognized that the principal or only cathode reaction in strong hydrochloric acid is the reduction of hydrogen ion to hydrogen gas and that the course of corrosion can be followed by measuring the volume of hydrogen evolved. The results of these studies are often difficult to assess in connection with the present work, primarily because limited attention was paid to structural factors and the alloys were or may have been

polyphase; the enhanced corrosion in such cases has been attributed to the presence of low hydrogen-overvoltage cathodes provided by the second phase<sup>6,7</sup>. However, certain pertinent information may be abstracted from the earlier studies. It was shown that the corrosion rate of high-purity material was markedly increased by the introduction into the acid of ions of certain metals (e.g., Pt, Cu) which cement out on the aluminum and provide cathodes of low overvoltage<sup>3</sup>. Since there may be significant quantities of one of these metals, copper, in the aluminum, the same result may conceivably be produced during the corrosion of aluminum leading to a corrosion rate which increases with time as the reaction is accelerated by one of its products (autocatalytic reaction). In 2N (7%) HCl, an accelerating rate was observed at 0.1% copper but not at 0.01%<sup>3,5</sup>. At a high copper level - 4% Cu in 0.9N (3½%) HCl - the cemented copper was visible as a dark powdery mass<sup>6</sup>; it is of interest to note the assertion in Reference 6 that the cemented copper was not in metallic contact with the aluminum and was thus a less potent accelerator of corrosion than the CuAl<sub>2</sub> precipitate particles in aged specimens.

In the present work, quantitative studies have been made of the autocatalytic reaction for copper contents from 0.002 to 0.06%. This reaction has been correlated with corrosion morphology, and the relation to the corrosion rate of the quantity and distribution of copper catalyst present has been considered.

## II. Procedure

A lot of high-purity aluminum containing 0.0021% Cu, 0.001% Fe and 0.003% Si (Alloy A) was alloyed with copper to yield aluminum containing 0.014% Cu (Alloy B) and 0.06% Cu (Alloy C). A few tests were made with low copper Alloy K which contained 0.0001% Cu, 0.0004% Fe and 0.0004% Si. Although fully satisfactory data for the other elements present are not yet available, the upper limit for any of these can be confidently estimated as 0.0005%. No significant differences among A, B and C were noted except for copper. None of the elements other than copper appears to be present in quantities sufficient to have an effect on general corrosion as great as the observed effect of the copper present in A, B and C. The only other heavy metals detected after close spectrographic examination were lead ( $< 0.0005\%$ ), cadmium ( $\leq 0.0003\%$ ) and silver ( $< 0.0001\%$ ). The effects of these elements on corrosion are being checked.

The acid was made up from a selected lot of 37½% CP hydrochloric acid containing 0.1 ppm heavy metals (mainly Pb), 0.05 ppm Fe and  $< 0.008$  ppm As and from water distilled from 1 megohm-cm demineralized water and believed to have contained negligible quantities of heavy metals influencing corrosion. Acid strength was adjusted to within 0.05% HCl of the stated value by using precision specific gravity measurements.

Test blanks 3/8 x 1-5/8 in. were sheared from cold rolled sheet 0.065 in. thick. Edges were finished by filing. The blanks were annealed in air at 645°C for 24 hours in aluminum boats and rapidly quenched in cold water. The high temperature anneal produced an average grain size

of 1/8 in. or larger and this minimized the contribution of intergranular corrosion to the total corrosion. It also produced what must have been a substantially homogeneous solid solution - for iron, copper or silicon, for example, the annealing temperature was 200°C or more above the solvus temperature. The quench is considered substantially to have preserved the high temperature structure except for the condensation of lattice vacancies into dislocation loops<sup>8</sup>. Slow cooling of aluminum is undesirable if a homogeneous solid solution is to be preserved since there are likely to be concentration gradients associated with precipitation or pre-precipitation phenomena involving the iron impurity and, in the present case, the copper in Alloy C.

Copper contents above 0.06% were not included since it was feared that slow precipitation reactions might occur on aging at room temperature. It did not appear that the as-quenched structure of the 0.06% alloy was unstable since two pairs of tests failed to show significant differences between specimens heat treated 3½ years earlier and specimens heat treated one or two days before.

Each test was preceded by a 6 minute etch in concentrated (37½%) acid (and by a rinse with test acid) to accelerate the removal of the high temperature film. Although this film is not protective, it was considered desirable to ensure a fixed initial condition by imposing through the etch a small amount of corrosion (0.01 - 0.02% weight loss). The concentrated acid etchant had the virtue of being available with lower metal ion content than other reagents which might conceivably have been used. That there will be substantial effects on subsequent corrosion as a consequence of cementation of foreign metals from the

etching solution on the aluminum surface is a clear danger in a system as sensitive as the one under study and has been demonstrated using dilute  $\text{H}_2\text{Cl}_2$  solutions<sup>9</sup>. Unfortunately, few instances of concern for and specification of reagent quality are recorded in the literature.

To follow the course of corrosion by determining the volume of hydrogen evolved, a weighed specimen was held without stirring in a calibrated 12 mm I.D. Pyrex tube closed at the top and initially filled with acid, the lower end of the tube being fixed below the surface of some acid in a beaker. The temperature control was somewhat coarse and occasionally erratic, and it was partly good fortune that the temperatures determined by monitoring lay within a 2° C range centered at 23.5°C for enough tests to permit determination of the corrosion parameters as functions of copper content at approximately this temperature. Vapor pressure and density data for the acid were available to correct the volume of gas collected to volumes of hydrogen under standard conditions (NTP). Tests were run to 90-100 ml NTP corresponding to 5% weight loss. The hydrogen collected was equivalent to a quantity of trivalent aluminum varying from 83 to 98% of the weight loss measured directly so that the hydrogen volume was a satisfactory measure of corrosion. The discrepancy tended to increase with exposure time; the 83% figure refers to a 38 day test. The solubility of hydrogen in hydrochloric acid would yield a discrepancy of 4% at saturation; the remainder was attributed to loss to the atmosphere.

Certain aspects of corrosion were studied with the specimen immersed in 100 ml of acid in a 400 ml beaker at  $24.0 \pm 0.3^\circ\text{C}$ . The rate of hydrogen evolution was viewed with the aid of a strong beam of light in a dark room and the

appearance of the specimen surface was followed with a hand lens and occasionally with a 15X-25X microscope. More than 10 alloys have been studied in over 200 intergranular and general corrosion beaker tests which guided the selection of conditions for hydrogen evolution experiments and which provided assurance that the characteristic features of general corrosion in hydrochloric acid reported here are indeed typical of high-purity aluminum.

The thinning of a number of specimens was measured and found to account for at least about 90% of the weight loss. This indicated that the contribution from the intergranular crevices to the total weight loss was small. Thus hydrogen volumes or weight losses reported here represented essentially only the average general corrosion.

### III. Results

#### A. Hydrogen Evolution Experiments

Representative hydrogen evolution data are plotted in Figs. 1 (16% HCl) and 2 (20% HCl). The curves could be resolved into (I) an induction period during which the rate of evolution was low and increased slowly, (II) a linear region of varying duration in which the rate of evolution was constant and had about the same value for all three alloys with acid of a given composition and (III) a region of slowly or rapidly accelerating evolution the character and inception time of which was a strong function of the copper content of the alloy or the solution.

It is important to note that experimental variables had to be maintained within narrow limits if the results were to be quantitatively significant. With an acid range of only 4% HCl, the rates varied from 0.1 ml/hr to 20 ml/min. At high rates the exothermic corrosion reaction



led to a temperature rise; by terminating the test at 100 ml, this rise was restricted to 0.7°C at the highest rate. In prolonged tests with Alloy C, the temperature rise contributed to the instability producing a violent reaction which raised the temperature of a beaker of 20% HCl to 60°C within 20 minutes after the onset of Stage III. Another experimental limitation was intergranular corrosion; in the tests on Alloy A in 20% HCl and in 16% HCl with 0.2 ppm cupric ion, this had progressed through the thickness of the specimen at a number of grain boundaries and the specimens would have fallen to pieces if the test had been prolonged.

In 16% HCl, Stage II was precisely linear for 11 days with Alloy A and for 2½ weeks with K. Eventually changes were noted; during the fourth week, the rate of evolution was 30% lower in K and 60% higher in A. These slow changes in rate were not considered necessarily indicative of a new stage of corrosion. Factors which may have been involved in the slow rate changes were: (a) changes in the actual surface area of the specimen, (b) an increase in acid strength due to preferential evaporation of its water vapor component, and to a small extent (c) a decrease in acid strength due to the consumption of hydrogen ion (this decrease is so small that acid initially 16.0% would still have been above 15.8% at 5% weight loss). There were no short period fluctuations in the rate (except for small ones associated with temperature fluctuations) such as those reported by Straumanis<sup>3</sup> who considered them a consequence of an inhomogeneous distribution of residual impurities in his aluminum (0.0003% Cu). Straumanis did not observe an extended linear stage of corrosion.

The characteristics of the hydrogen data are considered further in the following sections.

#### 1. Correlation with Morphology

The concentrated acid etch began the work of undercutting the high-temperature film as evidenced by the appearance of scattered crystallographically etched patches. Etching continued in the test acid; for Alloy A, the surface was almost fully etched after periods ranging from 1½ days in 1% HCl to 4 hours in 26% HCl. The time required for the surface to appear fully etched was about the same as the duration of Stage I. The peeling and floating off of the oxide film<sup>10</sup> was readily observable in acids below 18% where the film remained in patches of substantial size (5-10 mm).

The linear Stage II was associated with macroscopically uniform crystallographic corrosion which appeared microscopically as a cubic step and pit pattern having a unit dimension in the surface of 10 microns and step or pit depths of a few microns. This surface structure, which appears in Fig. 3 as the fine background etching, had less roughness but appeared basically similar to the 5 micron "block structure" noted by Roald and Streicher<sup>7</sup> for 20% HCl. Any variation in rate of attack with grain orientation would not appear as a prominent feature in the present work because of the orientation texture of the coarsened grains. With almost uniform thinning and a surface fine structure which remains substantially the same, the surface area can, once the surface structure has been established, remain approximately constant as the specimen thins. This point is significant in connection with the constant rate in Stage II; for a corrosion rate constant over the large

intervals observed for Alloys A and K in 16% HCl, a constant surface area is a necessary condition.

Stage III of accelerating corrosion rate was associated with the nucleation and growth of regions of localized corrosion which were superimposed on the uniform etching. The time at which localized corrosion had progressed far enough to be visible with a hand lens was slightly beyond the beginning of Stage III, as indicated by arrows in Figs. 1 and 2. The localized corrosion took the form of pits (Fig. 3a) or trenches (Fig. 3b); it varied in extent from one region to another but its distribution was unexpectedly uniform for an unstable reaction. The small range of pit or trench sizes observed at any one time indicates that the localized corrosion was initiated at many sites within a short time interval. The trenches are the "angular chasms" noted by Roald and Streicher. In both types, the depth was  $1/2$  to  $3/4$  the (narrow) dimension in the surface. Both were bounded by cube planes. The trenches resulted from preferential growth in the direction of the surface trace of one of the cube planes. The trenches were sometimes remarkably straight but usually they were jogged and so would appear to curve at low magnification as shown in Fig. 3b.

It is to be noted that the pit or trench was the source of a stream of hydrogen bubbles and hence contained the cathodes as well as the anodes of the localized corrosion reaction.

## 2. Significance of the Induction Period

A few weight loss measurements for short beaker exposures of Alloys A and C in 20% HCl were available for comparison with the corrosion indicated by the volume of

hydrogen collected. Conclusions had to be drawn cautiously since the duration of Stage I appeared to be the most variable aspect of the corrosion behavior. For Alloy A, weight losses (averages of three specimens) were equivalent to hydrogen volumes of 1 ml at 8 hours and 7 ml at 45 hours. Comparison with the actual volumes of 0.05 and 8 ml observed in the hydrogen experiment (Fig. 2) suggested that in the early part of Stage I the hydrogen volume represented an abnormally low fraction of the true weight loss. On the other hand, if the induction period had been absent and the corrosion rate indicated by the Stage II slope had been in effect at zero time, the hydrogen volumes would have been substantially higher than the weight loss equivalents - 2 ml at 8 hours and 11 ml at 45 hours; thus there was truly an initial stage of low corrosion rate. The presence of this stage may have been nothing more than a reflection of the fact that the area undergoing corrosion was increasing as etching progressed to cover the specimen surface, as noted in the previous section.

### 3. Quantitative Description of the Data

The linear Stage II was considered to represent the intrinsic corrosion rate of the solid solution. The rate in this stage was expressed as:

$$dV/d(t-t_0) = k_1 \text{ (Equation 1)}$$

where  $V$  is the volume of hydrogen collected up to time  $t$ ,  $t_0$  is the time intercept of the line, and  $k_1$  is its slope. The parameters were evaluated from expanded linear plots.

The Stage III acceleration began only after some Stage II corrosion had occurred and the magnitude of the acceleration increased sharply with copper content; this stage was considered to represent the acceleration of

corrosion by the copper already introduced into the solution. The hydrogen volume eventually rose exponentially with time. This behavior superimposed on the intrinsic corrosion yields for the Stage III rate:

$$dV/d(t-t_0) = k_1 + k_c V \text{ (Equation 1a)}$$

When  $V$  is large enough so that  $k_c V \gg k_1$ , Equation 1a may be written  $d(\ln V)/d(t-t_0) \approx k_c$  so that a plot of  $\ln V$  versus time will be linear with slope  $k_c$  if Equation 1a gives a correct description of the behavior. That this is so at sufficiently large  $V$  is shown in Fig. 4 for two tests. To evaluate  $k_c$  where it was not sufficiently large in comparison to  $k_1$ , an allowance had to be made for the contribution of  $k_1$  to the total rate. Since the  $k_c V$  rate is directly proportional to the total amount of corrosion already suffered (which indicates both that the accelerating agent is in the corrosion product and that it is not consumed), the reaction is correctly described as "autocatalytic."

It is important to note that the integrated form of Equation 1a did not correctly describe Stage II or the transition from Stage II to Stage III. The situation can be described by stating that  $k_c$  was small or zero during the linear stage and increased in a transition region to the constant value characteristic of the latter part of Stage III. For example with Alloy B in 16% HCl (Fig. 1), if the final  $k_c$  had been in effect early in the test the autocatalytic reaction would have been readily recognized when  $k_c V$  became equal to  $k_1$  at  $V = 1$  ml, which was patently not the case. Thus the autocatalytic reaction did not arrive on the scene until corrosion was already well under way. The characteristic inception time for its onset is discussed below.

With Alloy A in 16% HCl containing 0.2 ppm cupric ion (Fig. 1), the acceleration of corrosion in the third stage was low and not apparently regular and was not considered in detail

#### 4. Variation of Corrosion Parameters with Copper Content

The three parameters describing the hydrogen evolution data in 16% and 20% HCl are presented in Table I as functions of copper content. The good reproducibility for  $t_0$  and  $k_1$  shown by the duplicate figures for Alloy K represented favorable conditions (simultaneous tests and a long linear stage) and would not apply to certain of the other tests where the brevity of the linear stage made it impossible to verify the constancy of the observed rate over an extended period. The data on Alloy C for a slightly higher temperature indicate a strong temperature dependence which is about the same for  $k_c$  as for  $k_1$ ; the ratio of the two  $k_1$  is consistent with more reliable results on Alloy K in 16% HCl which indicated that  $k_1$  would double for a temperature rise of  $5\frac{1}{2}^\circ\text{C}$  (equivalent to an activation energy of 22,000 cal/mole). The differences in mean test temperature for the data in Table I were  $1.0^\circ\text{C}$  at most and could not therefore have been responsible for differences of more than 15% between the  $k_1$  for different alloys.

No systematic variation of  $k_1$  with copper content was apparent, and the only conclusion possible was that the intrinsic rate varied little if at all from one alloy to another.

Both  $t_0$  and  $k_c$  were functions of the copper content. The tendency for  $t_0$  to decrease with increasing copper did not produce sufficient variation in this parameter to make it of major importance so that it is fair to state that the

influence of copper was almost entirely exerted through its effect on the autocatalytic constant,  $k_c$ . The 30- to 100-fold increase in  $k_c$  for a 4-fold increase in copper content (Alloys B and C) is noteworthy. Since  $k_c$  was not proportional to copper content, the autocatalytic rate was not in general proportional to the amount of copper introduced by corrosion although this was true in any one test.

In the beaker tests in 1% to 26% HCl, the autocatalytic acceleration was observed to increase substantially with increasing acid strength. Thus the data in Table I for Alloy B, which show the reverse, are not typical in this respect.

Comparison of the present data with earlier work is generally pointless. For example, Straumanis'<sup>3</sup> conditions are known to be different in that he used a machined surface which was rotated in the acid, and there are unknown factors in regard to his test temperatures, acid purity and specimen homogeneity.

#### B. Inception Time for the Autocatalytic Reaction

##### 1. Determination by Hydrogen Evolution

In Alloys B and C, the onset of the autocatalytic reaction led in a short time to a high corrosion rate (Figs. 1 and 2) and was therefore readily detected by visual observations of the hydrogen evolution rate in beaker tests. The inception times, plotted in Fig. 5 as functions of acid strength from 1% (0.5N) to 26% (8.1N), increased with decreasing acid strength and rose sharply in a narrow range of acid concentrations. The relatively small scatter of the data was unusual for an unstable phenomenon. The long inception times at lower acid strengths were not due to the reduction of acid

strength as hydrogen ion was consumed during corrosion - this difficulty was mitigated where required by increasing the volume of test acid to 1000 ml so that even for the test in 1% HCl the acid strength at the end of the test would have been only 7% lower than its original value. With prolonged exposure there was in addition a compensating factor in the tendency for the acid strength to rise (about 5% per month for 1% HCl) due to the preferential evaporation of its water vapor component. Thus in no test would the change in acid strength have been more than a few percent of its original value.

Straumanis<sup>3</sup> measured inception times in 2N (7%) HCl by a similar method. His values varied from 1 day for 0.1% Cu to 2 hours for 5% Cu, consistent with the data in Fig. 5.

## 2. Determination by the Appearance of Localized Corrosion

A more sensitive index of the onset of the autocatalytic reaction when the acceleration was low was the time when the pit or trench pattern could be just detected on the specimen surface. Some inception times determined in this way were available for Alloys B and C; these times were substantially earlier than those given in Fig. 5 only in the weaker acids (in 7% HCl, for example, two days earlier for Alloy C and one week earlier for Alloy B). The more sensitive method could be extended to alloys of low copper content. In Alloy A the inception times corresponding to the incidence of localized corrosion were 3/4 day in 26% HCl, 3 1/2 days in 20% HCl, and 6 days in 18% HCl. There was no recognizable localized corrosion within 58 days in 16% HCl. Thus the inception time for A varied with acid strength in a fashion similar to the variation for B and C shown in Fig. 5; the lower the copper



content the higher lay the range of acid strengths at which the characteristic variation became manifest. For Alloy K (0.0001% Cu), the inception times in 18% and 20% HCl were about three times those for Alloy A (0.0021% Cu) so that even the small amount of copper in A appears to have been responsible for an autocatalytic reaction. In the absence of data for copper contents below 0.0001%, it is not legitimate to infer that the occurrence of localized corrosion in K is indicative of an autocatalytic reaction involving the copper (or other) impurity in this alloy; the observation that an addition of cupric ion to the acid led to the early appearance of a localized corrosion pattern (Fig. 1) suggests that the pattern in K may have been due to the small amounts of heavy metal ions in the test acid.

The localized corrosion was invariably of the trench type in K and A and invariably of the pit type in C while B showed trenches in 16% and stronger acid and pits in 14% and weaker acid. Thus with increasing copper content there was a transition in the vicinity of 0.01% Cu from trenches to pits.

### 3. Condition for Inception of Autocatalytic Reaction

Table II shows the weight losses at the times when the autocatalytic reaction was first detectable for those cases where this information was available from hydrogen or beaker tests. The calculated weight of copper, originally in the specimen, which was introduced into the acid by this weight loss is also given. The latter quantity shows substantially less variation and very little variation in view of the fact that the  $k_c$  (determined later in the test) varied by three orders of magnitude. It therefore appears that the condition for the autocatalytic reaction to begin is that a quantity of

copper of the order of one microgram shall have been introduced by corrosion. One microgram is equivalent to half a monolayer of metallic copper based on the nominal surface area.

This conclusion is consistent with the results of scratch tests. A scratch through the oxide film of a specimen of Alloy C made with a pointed glass rod immediately after immersion in 14% HCl did not lead to visible localized attack. The slight additional hydrogen evolution associated with the scratch ceased entirely within 10 hours. On the other hand, a scratch made at a time 31 hours later, when some copper had been introduced by corrosion (this was shortly before the inception of the autocatalytic reaction), led to persistent hydrogen evolution and the development of pits at several sites along the scratch. This behavior suggests that the absence of sufficient copper for catalysis rather than the absence of strong local cells was responsible for the delayed inception of the autocatalytic reaction.

The test acid contained heavy metal ions - about 10 micrograms for 16% acid. Although these were present from the start of the test, the onset of the autocatalytic reaction had in every case to await the introduction of a smaller amount of copper from the specimen. This point is considered later in connection with the effect of a cupric ion addition (Section IV-3).

#### C. Potential and Coupling Test

The relative solution potentials (as measured with an electrometer-tube meter) and the effects of coupling were explored for a specimen of Alloy A (0.0021% Cu) compared with one (having the same area) of Alloy C (0.06% Cu) in 16% HCl. The high copper specimen was initially 50-60 mv

cathodic. After 15 minutes, the two were coupled through an 0.8 ohm resistance. Period measurement of the uncoupled (open circuit) potential difference showed a non-systematic drift, the high copper specimen varying from 50 to 160 mv cathodic. The open circuit potential difference did not drift at an appreciable rate with time and was not affected by agitation; it did not change noticeably with the onset of the autocatalytic reaction in the C specimen.

The current density while the two were coupled remained for two days near  $0.008 \text{ ma/cm}^2$ ; the potential difference then was about 0.06 mv. The current density was higher by a factor of 50 on the fourth day when the autocatalytic reaction had started in the C specimen. At this time, 90% of the polarization on coupling was associated with the Alloy A anode (this was determined at a point when C was 72 mv cathodic to A which was 960 mv anodic to a saturated calomel electrode at  $24^\circ\text{C}$ ). The effect of coupling on the high copper C specimen was marked - the inception time for the autocatalytic reaction was increased by a factor of four and the rate of nucleation of localized corrosion sites was greatly reduced so that the first pit had grown to 2 mm diameter before another pit was nucleated (cf. Fig. 3a).

The features of these observations listed below were significant in relation to other aspects of the present work. It is to be noted that it is not likely that the current density for the coupled specimens was uniform over either cathode or anode.

(1) Before the autocatalytic reaction, copper had previously produced little or no effect on the corrosion

rate (i.e., on  $k_1$  in Table I) but it produced here a large effect on the solution potential. The magnitude of the effect is apparent from the fact that more than 1% copper is required in a  $\text{NaCl-H}_2\text{O}_2$  solution to make the potential of an aluminum solid solution 100 mv more noble<sup>11</sup>.

(2) Despite the large open circuit potential difference, the current flowing between the coupled specimens was small (strong polarization). This current at the anode was equivalent to only 1/4 of the intrinsic (uncoupled) corrosion rate indicated by the value of  $k_1$  for 16% HCl.

(3) That the autocatalytic reaction at the cathode was delayed was to have been anticipated since the rate of attainment of the minimum amount of corrosion required for its onset (Section III-B-3) would have been reduced by the current flowing. However, the observed effect on the autocatalytic reaction in Alloy C was quite out of proportion to the small effect on intrinsic corrosion implied by the low current density.

#### IV. Discussion

Before the start of the autocatalytic reaction, the presence of copper in the aluminum has little influence on corrosion although it does affect the solution potential. The effect of copper content on induction time may be related to the properties of the oxide film rather than of the solid solution and hence may be specific to the surface treatment employed which does not completely remove the high temperature film. Thus the following paragraphs on the role of copper deal almost exclusively with the autocatalytic reaction which does not appear to depend on any characteristic of the specimen except its copper content, at least in the present alloys where no

other impurity having an analogous effect is believed present in important quantities.

A. Practical Significance of the Inception Time

Although the inception time of the autocatalytic reaction will be long with low copper contents or acid strengths, there is reason to believe this reaction will occur eventually even beyond the range of variables investigated in the present work. Without knowledge of the delayed aspect of this reaction, the occurrence of this reaction and the principal effect of a copper impurity might remain undetected. Such a case was Shaumanis<sup>3</sup> failure to observe the effect of a 0.01% Cu addition to a high-purity aluminum in 2N (7.0%) HCl in a test terminated after one week - the present work indicates a large effect but only after six weeks. That a prematurely terminated test can be grossly misleading is illustrated by comparing the curves in 16% HCl for Alloys A and B in Fig. 1; although the two are hardly distinguishable up to 75 hours, at 85 hours the difference is unmistakable, and at 95 hours the rates differ by two orders of magnitude. If the inception of the autocatalytic reaction requires an amount of corrosion sufficient to introduce a certain quantity per unit area of copper as corrosion product (Section III-B-3), the inception time should vary inversely with copper content and inversely with  $k_1$ , the existence of the induction time being neglected. Quantitatively, this is reasonably close to the actual case only for Alloys B and C above 14% HCl.

Since the autocatalytic reaction proceeds simultaneously at many sites on the specimen (Fig. 3a), the inception time and the value of  $k_c$  would be expected

to be substantially independent of specimen area. On the other hand,  $k_1$  should be proportional to the area.

#### B. Movement of Copper During Corrosion

The following broad description of the movements of the copper in the hydrochloric acid corrosion of aluminum is constructed with the support of visual evidence obtainable when there are large quantities of copper in the aluminum<sup>6</sup> or the acid<sup>12</sup> and is consistent with the thermodynamic data given in Table III. Copper ions or the chloride complex anion, whatever their source, tend to be reduced to metallic copper on the specimen surface. The metallic copper constitutes the cathode of a local cell and is itself cathodically protected against corrosion until it is undercut by corrosion of the underlying aluminum. Once freed, the small masses of copper undergo corrosion in the oxygenated acid to form cupric ion. The cycle will then repeat. There is no reason to believe the situation is different in the present experiments where copper contents are low and evidence of the presence of metallic copper on the specimen and in the solution is not readily obtained visually.

#### C. The Effect of Adding Cupric Ions to the Solution

One striking result of the present work is that copper originally in solid solution in the specimen is ultimately much more potent in its effect than copper ions originally in the acid. This is illustrated by the comparison of data for 16% HCl in Fig. 1 and Table I. With Alloy A, the addition to the acid of 0.2 ppm cupric ion (a total of 54 micrograms) produced a substantial and early increase in the corrosion rate. However a much higher corrosion rate was ultimately associated with the addition

of copper to the specimen as represented by the test on Alloy B. In comparison with the curve for the cupric ion addition, the curve for Alloy B shows a higher slope starting at 85 hours; at this point only 1.7 micrograms of copper had been introduced by the corrosion of B as compared with the much larger quantity of cupric ion added before the beginning of the other test. Beyond this point, the rate for Alloy B becomes an order of magnitude higher when much less than 54 micrograms of copper have been introduced by corrosion.

It is likely that the quantity of copper ion in the acid at any one time is small so that the explanation of the large difference between the two cases in the stimulation of corrosion is to be sought in the manner in which metallic copper is deposited on the specimen surface. The difference is so large as to appear explainable only if the copper is primarily on top of a film in one case and primarily in metallic contact with the aluminum in the other, as outlined in the following section.

For heavy metals other than copper, the situation may be quite different; Straumanis<sup>3</sup> noted strong hydrogen evolution after short times for additions of a platinum solution containing only 0.1 microgram of platinum to 2N (7%) or 5N (16.7%) HCl.

#### D. Mechanisms of Acceleration of Corrosion by Copper

Attention is focussed on the situation where the original oxide film has been replaced by a high-resistance thin film characteristic of the acid environment. The existence of such a film is implied by the moderate corrosion rates observed in a system so unstable thermodynamically. It may be noted that this film can not be the

same substance as the aluminum hydroxide formed by precipitation; this hydroxide has a solubility product of  $10^{-33}$  and the strong acids used can retain in solution many times the total quantity of aluminum in the specimen. The precise nature of the local cell action, which will be considered in more detail in a subsequent paper<sup>1</sup>, is not essential to the argument here.

Cupric ions originally in the solution will be attracted to the local cathodes; these cathodes are presumed to be filmed and the ions will be reduced to metallic copper on top of the film. The cupric ion content of the acid is too low to form an effective aluminum-copper couple - the copper accelerates corrosion because it forms a cathode surface of lower hydrogen overvoltage than the original surface. With the metallic copper overlying the film, the corrosion rate is still limited by the high electronic resistance of the film which is in series with the local cell. It has actually been observed that a visible deposit of copper can be present in an aggressive medium without a strong influence on corrosion<sup>13</sup>. When the patch of copper freed from the specimen and oxidized to cupric ion the initial situation is recovered, the local cell having lost its catalyst. Cycles of this type lead to increased rates of uniform corrosion but do not account for the (trench-type) localized corrosion also produced by cupric ion additions. Localization requires that the active regions remain active. For this to happen, the local cell must acquire catalyst faster than it loses it, and the local cell action must then be different in some respect from the action described above. Since localized corrosion is observed to be associated with



intense local hydrogen evolution it is reasonable to suppose that the localized corrosion cells are different because they have copper cathodes in metallic contact with the aluminum. The intense activity is attained in the absence of the high resistance film. The higher fields these cells produce in the acid may be related to their greater ability to capture or retain catalyst. In the case where cupric ion is added to the acid, the growth in size of the regions undergoing localized corrosion requires the acquisition of copper catalyst from the acid where the copper ion concentration is low, so that no more than a moderate acceleration of corrosion is possible; this is consistent with the results shown in Fig. 1.

The reduction of copper ions to elemental copper in metallic contact appears possible through the formation of the cuprous chloride complex anion which will migrate to the anode, presumed film-free, and which can be reduced there by aluminum.

Copper introduced by corrosion of the aluminum solid solution is directly at a presumably film-free surface. As compared with the previous case, it is supposed that a greater fraction of the copper introduced will deposit in metallic contact. In this event, a strong local cell can acquire additional effective catalyst rapidly, which accounts for the high acceleration of corrosion which is characteristic of this case. A certain fraction of the copper catalyst in metallic contact transfers when undercut or before to other areas in metallic contact (presumably in the same pit); if all this catalyst passed to cupric ion in the

body of the acid, it would be almost lost as a corrosion stimulator which is inconsistent with the observation (Section III-A-3) that the autocatalytic rate  $k_c V$  depends on the total quantity of corrosion product. The observed lack of proportionality between  $k_c$  and the copper content of the alloy suggests that the fraction of copper retained in metallic contact varies with copper content.

The inception of the autocatalytic reaction requires the introduction of a minimum quantity of copper equivalent to something less than a monolayer. This is to be expected if the copper deposits on the aluminum surface near its point of entry since the metallic copper will not constitute a strong cathode until it forms a patch of a certain minimum size. In the coupling test (Section III-C), a cathodic current too small to have a major influence on the intrinsic corrosion rate greatly increased the inception time presumably because it tended to retain the copper atoms at the sites where they first settled and thus made more difficult their aggregation into patches of the minimum size.

#### E. Significance of trenches and pits

The total surface areas of the pits or trenches in several hydrogen test specimens were estimated by painstaking microscopic examination. Since the pits or trenches have plane walls, no uncertainty due to surface roughness was involved in the estimates. All available corrosion data are given in Table IV. The pit or trench area varies very little in comparison with the other quantities. The last column shows the hypothetical copper density in the pits or trenches as calculated on the basis that all the copper introduced or added is associated with localized corrosion and that this copper is distributed over the

whole localized corrosion area. 0.2 microgram per  $\text{cm}^2$  would be equivalent to a monolayer of elemental copper. Even if the calculated copper densities are quite far from the actual ones, the figures suggest that the pits in Alloy C contain sufficient copper to form cathodes in metallic contact at every part of the pit, which accounts for their ability to grow in all directions simultaneously. It is supposed on the other hand that the trenches, especially in Alloy A, have insufficient copper in metallic contact to form even a monolayer except over a fraction of their surface and that this copper is concentrated at the end of the trench where growth is occurring. That the addition of a large amount of cupric ion to the solution (the last entry in Table IV) yields the trench mode is in line with this view granted the previous argument that only a small fraction of the added cupric ion will end up in metallic contact participating in localized corrosion. The hydrogen evolution rates shown in the table are produced mainly by the localized corrosion; the large differences in these rates are considered to represent primarily differences in the number of local cells involving copper cathodes in metallic contact rather than different local cell activities.

#### F. Intergranular Corrosion

Although this phenomenon will be treated in detail in a subsequent paper<sup>1</sup>, some remarks are pertinent here.

In the present work, the grain boundary is hardly more than a lattice defect; there may be some solute atom segregation but there is no local disturbance comparable to the one produced by grain boundary precipitation in the high copper alloys.<sup>14</sup> Thus the grain boundary corrosion

cell will not be qualitatively different from the local cells in the grain body (which may also involve lattice defects), and the mechanisms of intergranular and general corrosion will be closely related. The study of general corrosion is of great value for the understanding of intergranular corrosion because the intrinsic and catalytic factors common to both types are much more readily demonstrated for general corrosion. The point derived from the present work which is important for intergranular corrosion is that the local cell at the grain boundary is a built-in strong cell and will be autocatalytically stimulated in alloys containing copper by a reaction akin to the autocatalytic reaction which occurs later within the grain body. It is proposed that the grain boundary has a higher intrinsic corrosion rate but truly high rates of penetration (i.e. millimeters per week) will not be observed in the absence of copper in the alloy. Since grain and subgrain boundary attack is known to be markedly accelerated by small cupric ion additions <sup>12,15,16</sup>, and since the general corrosion work indicates greater catalytic efficiency when the copper is introduced from the alloy, one would expect significant autocatalytic effects in grain boundary corrosion at low copper levels. The four alloys of the present study exhibited intergranular corrosion rates which increased markedly with increasing copper content. It is consistent with the present view that intergranular attack is very slow but not absent when the copper content is reduced to 0.000006%. <sup>16</sup>

In the high copper alloys, intergranular corrosion could be displayed clearly only in a narrow range of acid strength. Fig. 5 shows, for Alloy B, the time required for intergranular corrosion to progress through the thickness

of the specimen at one or more grain boundaries (this was the measure of the rate of intergranular attack). This time could be determined in 12% and 14% HCl where it was not excessive and yet was earlier than the inception of autocatalytic general corrosion. At acid concentrations of 16% and above, the autocatalytic reaction became general before this time, and then the grain boundary attack was almost lost in the general catastrophic corrosion. With Alloy C, to observe the completion of intergranular attack it was necessary to go to 1% HCl.

Under certain circumstances the presence of grain boundaries may have some influence on general corrosion. As an anode, the grain boundary initially places under cathodic protection the adjacent strips of grain body. In a fine-grained specimen, this could produce the retardation of the autocatalytic reaction that was observed in the coupling test (Section III-C). In the present work the grain size was large and nothing was observed to challenge the belief that the general corrosion was to a first approximation independent of the presence of the boundaries. Once an intergranular crevice had been established, the cathode of the grain boundary cell lay within the crevice (hydrogen was evolved there); this provided more direct evidence that the two reactions were proceeding independently at that time.

#### G. Behavior of Aluminum in Other Corrodents.

In some corrodents other than hydrochloric acid, the copper impurity may be involved in a manner related to the one observed here. The present work is able to display certain effects at high magnification and may facilitate the recognition of copper impurity effects in cases where they are not readily found unless specifically

sought. That the corrosion of aluminum can be strongly influenced by copper ions in the corrodent is generally recognized. That larger effects can be produced by smaller amounts of copper introduced by corrosion of the specimen is not generally known. This is significant because many studies deal with commercial or refined aluminum containing moderate to large percentages of copper by the standards of the present work.

One case of interest is pitting corrosion in nearly neutral chloride solutions. The theory of Edeleanu and Evans<sup>17</sup> proposes that the fraction of soluble product increases at the anode as the pH falls as a result of hydrolysis of the corrosion product and that this unstable situation persists until hydrogen is evolved at the pit raising the pH so that insoluble product is produced (filming). The present work suggests that copper introduced during pit formation will be important under certain circumstances since it can influence the discharge of hydrogen ion from the weak hydrochloric acid solution in the pit.

Preliminary tests with unetched specimens of the present alloys in a NaCl-  $H_2O_2$  solution at pH 4.9 produced some pits up to 0.2 mm but revealed no significant variation with copper content. The behavior was consistent with the theory of Edeleanu and Evans except that gas evolution and pit growth continued for several days or a week after the gas evolution had started and before all activity ceased as the growing mound of aluminum hydroxide finally covered the pit completely.

Hydrogen evolution will permit a substantial increment in size of the pit, if it does not lead to immediate

stifling, because in its absence the pitting reaction is under cathodic control.<sup>18</sup> The presence of a copper catalyst would be expected to initiate the discharge of hydrogen ion at a smaller pit size and to prolong the duration of the discharge so that the net effect anticipated is not clear. The copper in the specimen would produce no significant effect if pit growth ceased before a sufficient amount of copper had been introduced. The substance of these considerations is that notwithstanding the negative preliminary results reported here, the possibility that copper introduced from the specimen will have important effects on pitting should not be overlooked in future work. That small additions of copper to the aluminum can enhance pitting in a variety of solutions has been observed.<sup>19</sup>

#### V. Summary

Quantitative and morphological aspects of the general corrosion of coarse-grained single-phase high-purity aluminum containing 0.0001 to 0.06% copper were studied in 1% to 26% hydrochloric acid.

1. Hydrogen evolution measurements in 16% and 20% HCl indicated three stages of corrosion. There was an initial slow stage the presence of which may not have been significant except in relation to the method of surface preparation. The second stage was one of macroscopically uniform corrosion at a constant rate which varied little if any with copper content. The third stage when observed was an acceleration of corrosion localized in pits or trenches and resulting from catalysis of the corrosion reaction by low hydrogen-overvoltage cathodes forming from the copper in the corrosion product. The effect of copper in the aluminum was exerted almost entirely in

this stage. The catalyzed rate was proportional to the total corrosion (quantitatively autocatalytic reaction) with a rate constant which increased by three orders of magnitude for a 30-fold increase in copper content.

2. The characteristic delay time for the inception of the autocatalytic reaction at  $\geq 0.002\%$  copper decreased with increasing copper content and with increasing acid strength (increasing intrinsic corrosion rate) so that this reaction began when a certain quantity of copper, of the order of the equivalent of a monolayer based on the nominal area, had been introduced by corrosion.

4. Raising the copper content from 0.002 to 0.06% while maintaining other elements constant resulted in a cathodic shift in corrosion potential of the order of 100 mv in 16% HCl even though the intrinsic corrosion rate was to a first approximation unaltered.

5. It was pointed out that the catalysis of the corrosion of aluminum by copper in the corrosion product may be significant under a wider range of conditions than has hitherto been recognized. The cases of intergranular corrosion in hydrochloric acid and of neutral chloride pitting were discussed.



## VI. Acknowledgements

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## References

1. O. P. Arora, G.R. Ramagopal and M. Metzger - to be published.
2. U. R. Evans, "Metallic Corrosion, Passivity and Protection," 2nd Ed., Arnold, London (1946).
3. M. Straumanis, Korrosion und Metallschutz 14, 1 (1938)
4. A. von Zeerleder and E. Zurbügg, Aluminium 20, 365 (1938).
5. M. Straumanis and N. Brakss, Korrosion und Metallschutz 15, 5 (1939).
6. G. Tammann and W. Boehme, Z. anorg. Chem. 226, 82 (1935)
7. B. Roald and M.A. Streicher, J. Electrochem. Soc. 97, 283 (1950).
8. P.B. Hirsch, J. Silcox, R.E. Smallman and K.H. Westmacott, Phil. Mag. 3, 897 (1958).
9. A. Quartaroli and O. Belfiori, Korrosion und Metallschutz 14, 7 (1938).
10. F. Keller and J.D. Edwards, Metal Progress 54, 195 (1948).
11. R.H. Brown, W.L. Pink and M.S. Hunter, Trans. AIME 143, 115 (1941).
12. M. Metzger and J. Intrater, NACA Technical Note 3281 (February 1955).
13. R.B. Mears and R.H. Brown, Industrial and Engineering Chemistry 29, 1087 (1937).
14. E.H. Dix, Jr., Trans AIME 137, 11 (1940).
15. M. Metzger and J. Intrater, Nature (London) 174, 547 (1954).
16. F. Montariol, Corrosion et Anticorrosion 6, 101 (1958).
17. C. Edeleanu and U.R. Evans, Trans. Far. Soc. 47, 1121 (1951).
18. R.H. Brown and R.B. Mears, Trans. Electrochem Soc. 74, 495 (1938).
19. E. Kühnrich, Korrosion und Metallschutz 14, Suppl. #1, 1(1938).

TABLE I

Corrosion Parameters as Functions of Copper Content

Percent HCl	Alloy	Percent Cu	Intercept Induction Time, $t_0$ , hours	Intrinsic Rate $k_1$ , ml/hr	Autocatalytic constant, $k_c$ , ml <sup>-1</sup>
16	K	0.0001	52	0.117	not observed
	K	0.0001	50	0.126	not observed
	A	0.0021	27.3	0.140	not observed
	B	0.014	21	0.17	0.17
	C	0.06	20	0.10	4.65
16 with 0.2 ppm Cu++	A	0.0021	8.0	0.31	not determinable
20	A	0.0021	15.3	0.24	0.02
	B	0.014	7	0.22-0.29	0.14
	C	0.06	4.6	0.23	15
	(C)	(0.06)	(2.9)	(0.31)	(21.5) (26°C)

Nominal temperature 23.5°C.

Specimen Surface area  $8.9 \pm 0.3 \text{ cm}^2$ .

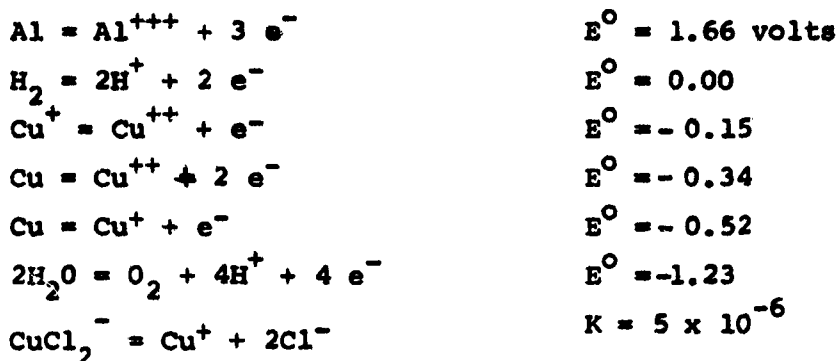
TABLE II

Weight Loss and Weight of Copper in the Corrosion Product at the Inception of the Autocatalytic Reaction

Percent HCl	Alloy	Percent Cu	Percent Wt. loss	Milligrams of Copper in Corrosion Product	$k_c$ from Table I
20	A	0.0021	1.4	0.5	0.02
	B	0.014	0.5	1	0.14
	C	0.06	0.1-0.2	1-2	15
16	A	0.0021	> 13	> 4	not observed
	B	0.014	0.9	2	0.17
	C	0.06	0.3	3	4.65
14	C	0.06	0.2-0.3	2-3	not measured

TABLE III

## Thermodynamic Data Pertaining to the Corrosion of Aluminum



W. H. Latimer, 2nd ed., Prentice Hall, New York, 1952,

"The Oxidation States of the Elements and Their Potentials in Aqueous Solutions."

TABLE IV

## Data for Estimating Relative Surface Density of Copper Catalyst in Regions Undergoing Localized Corrosion

Percent Copper	Percent HCl	Type	Rate of $\text{H}_2$ Evolution ml/min	Surface Area of Pits or Trenches $\text{cm}^2$	Micrograms of Copper in Corrosion Product	Hypothetical Micrograms Cu per $\text{cm}^2$ of Pit or Trench*
0.06	16	Pits	6.8	16	52	3.2
	20	Pits	29	28	51	1.8
0.014	16	Trenches	0.26	13	11	0.9
	20	Trenches	0.22	19	11	0.6
0.0021	20	Trenches	0.022	20	1.8	0.09
0.0021	16	Trenches	0.023	25	1.8	0.07
	(0.2 ppm $\text{Cu}^{++}$ )				(54)	(2.1)

About 5% weight loss in all tests.

\*A fictitious surface density which assumes all the copper indicated in column seven is associated with pits or trenches and is uniformly distributed over the area in column six.

Captions for Figs. 1, 2, 4, 5

- Fig. 1. Hydrogen Evolution Data for 16% HCl Which Compare the Effect of Adding Cupric Ion to the Acid with the Effect of Adding Copper to the Alloy. The arrows indicate the times at which the localized-corrosion trench pattern was detectable with a 5X hand lens.
- Fig. 2. Hydrogen Evolution Data at Three Copper Levels in 20% HCl Showing an Acceleration of Corrosion Which is Greater and Occurs Earlier the Higher the Copper Content.
- Fig. 4. Semilogarithmic Plot of Hydrogen Data for Two Tests Showing That  $d(\ln V)/dt$  is Constant for Sufficiently Large V.
- Fig. 5. The Inception Time for the Autocatalytic Reaction for Alloys B and C and the Intergranular Corrosion Time for Alloy B as Functions of Acid Strength. The inception time is the time at which the rate of hydrogen evolution as estimated visually became of the order of 10 ml/hr.

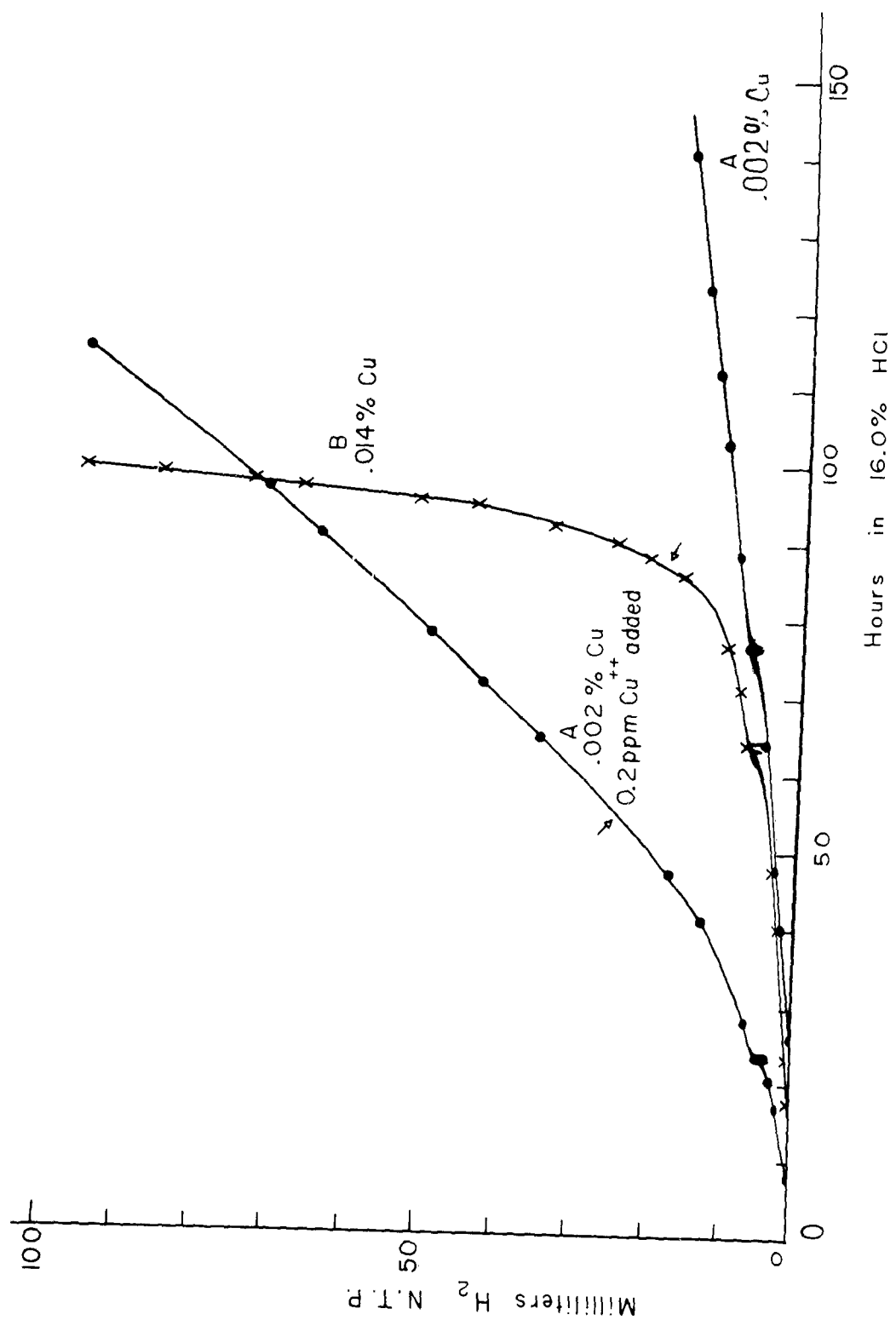


FIG. 1

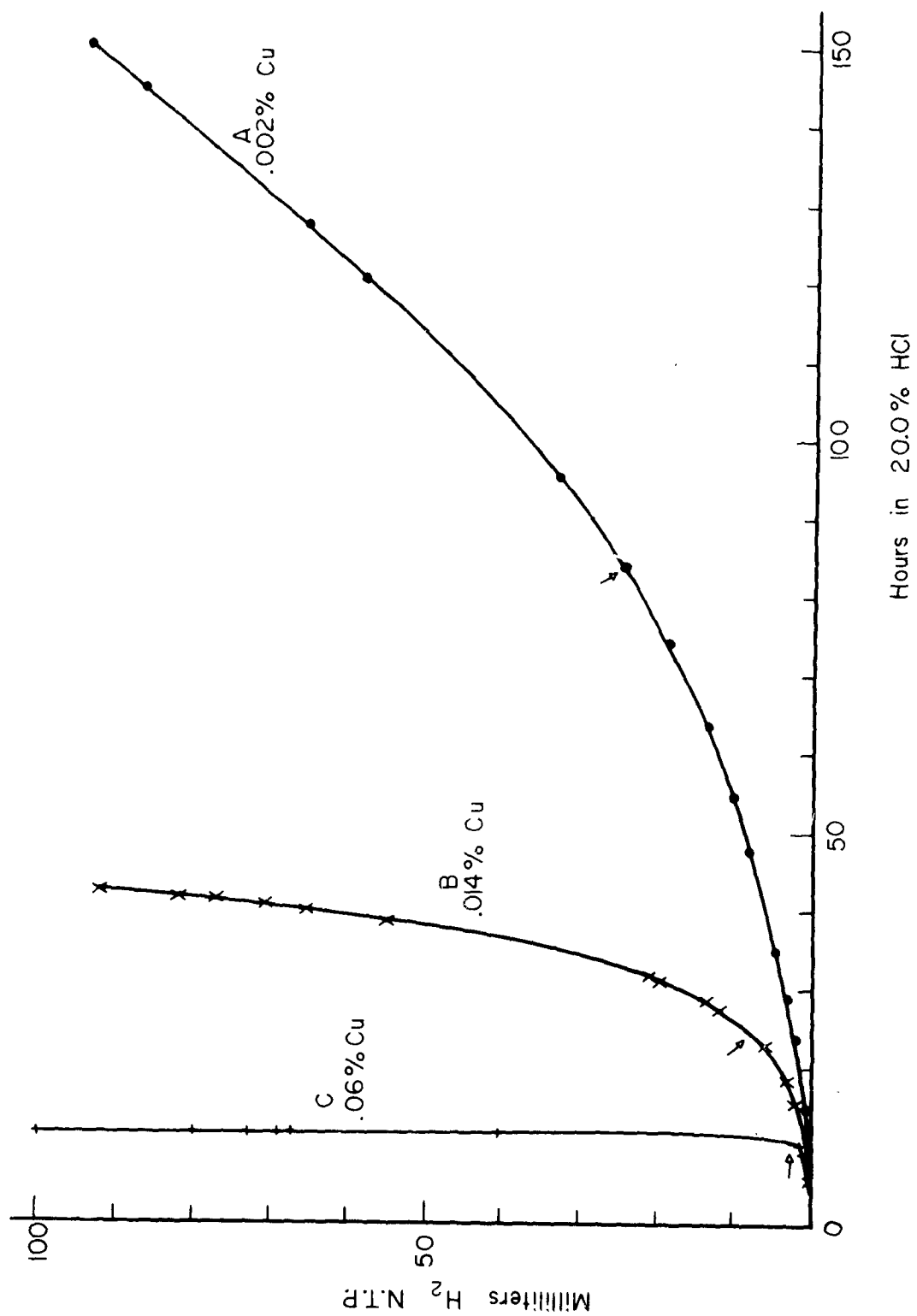


FIG. 2

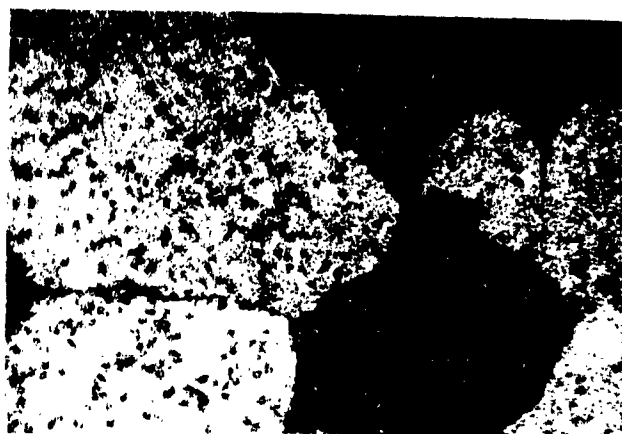


Fig. 3 Morphological Features of Corrosion. Diffuse illumination, 26X.

- (a) - above - Alloy C (0.06% Cu) after 4 days in 7% HCl. Weight loss 1.3%. Pit-type localized corrosion superimposed on uniform corrosion. There is shallow grain-boundary attack.
- (b) - below - Alloy A (0.002% Cu) after 9 days in 20% HCl. Weight loss 5.4%. Trench-type localized corrosion superimposed on uniform corrosion. Many grain boundaries (including three in this field) have been corroded through the thickness of the specimen.

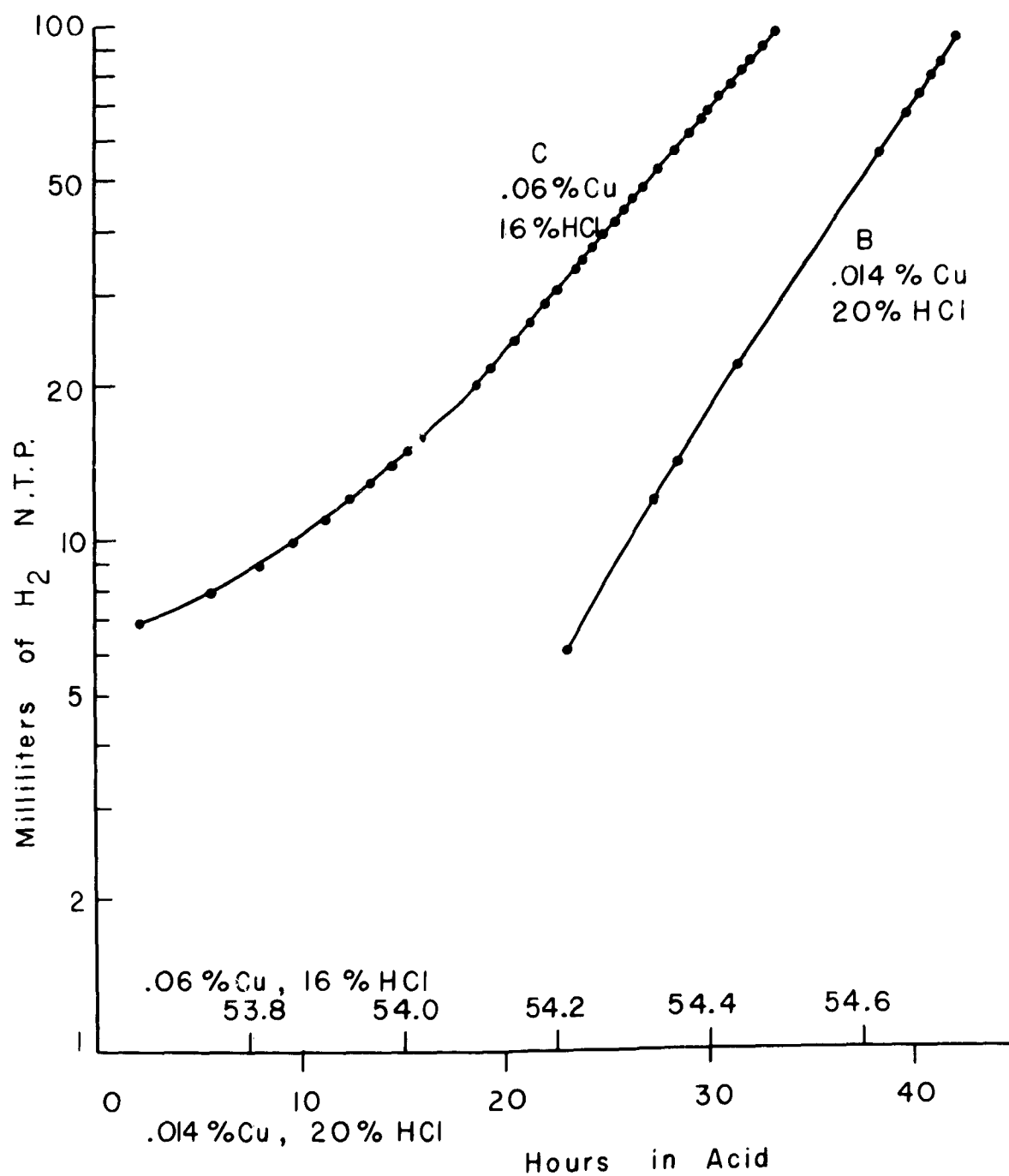


FIG. 4



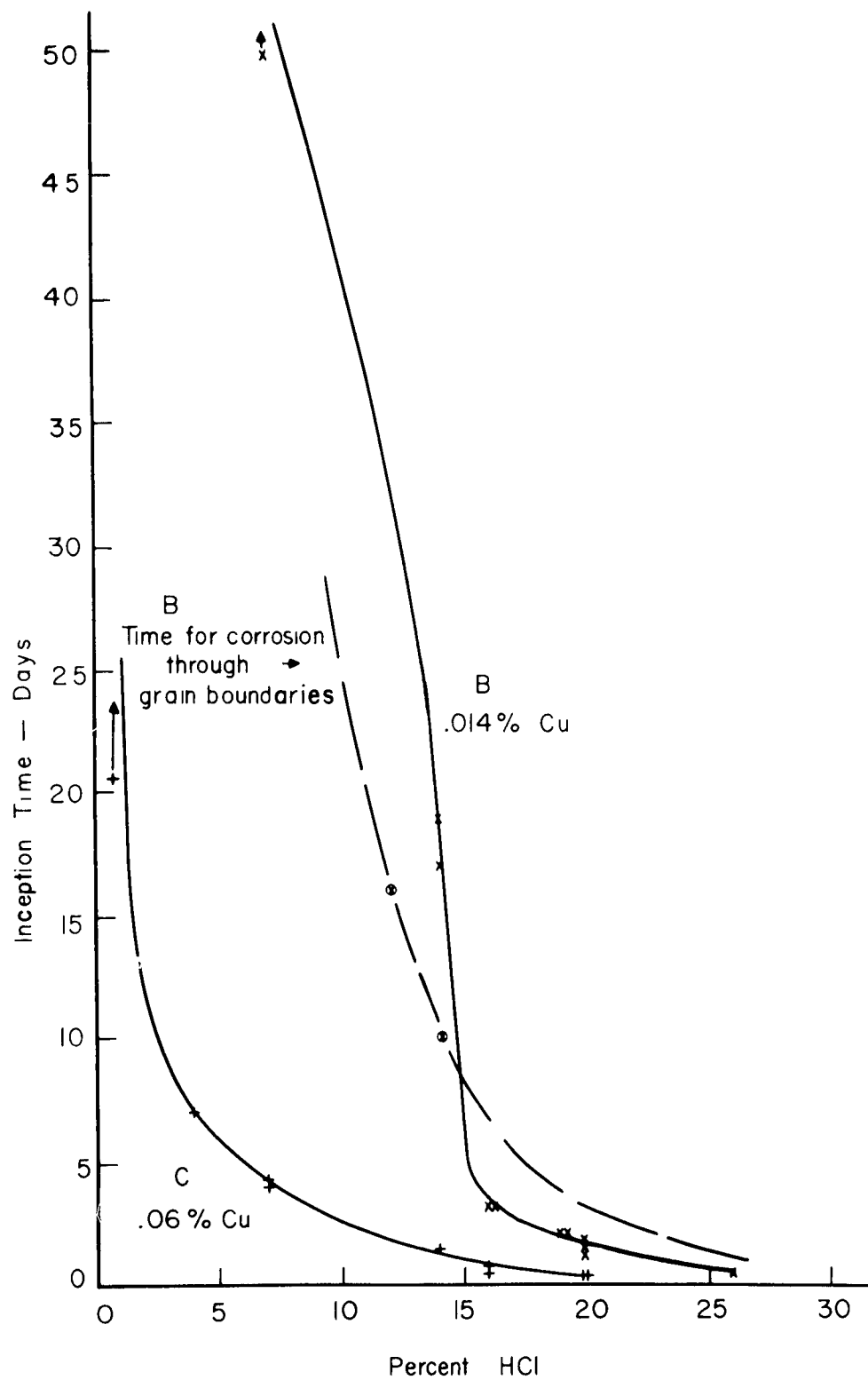


FIG. 5